

[Found: C, 62.74; H, 4.20; Ti, 6.71. $[(C_6H_4(O)CHO)_2Ti[(C_6H_5)_2PO_2]_2]$ requires C, 62.99; H, 4.14; Ti, 6.63%].

Other compounds were prepared similarly.

References

- SCHUMANN, H., JUTZI, P., ROTH, A. & SCHAUER, E., *J. organometal. Chem.*, **10** (1967), 71.
- ISSLEIB, K. & WALTHER, B., *J. organometal. Chem.*, **10** (1967), 177.
- RIDENOUR, R. E. & FLAGG, E. E., *J. organometal. Chem.*, **16** (1969), 393.
- FELD, R., *The organic chemistry of titanium* (Butterworths, London), 1965, 140.
- PANDIT, S. K., NERLEKAR, P. G. & GUPTA, J., *Indian J. Chem.*, **5** (1967), 121.
- GREENWOOD, N. N., *J. chem. Soc.*, (1960), 1130.

Adducts of 1-Phenylazo-2-naphthols with Fe(III) Chloride

N. THANKARAJAN & K. KRISHNANKUTTY

Department of Chemistry, University of Calicut, Calicut

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1-Phenylazo-2-naphthols form adducts of the type $FeCl_3.L_2$ with iron(III) chloride. Infrared spectral studies show that the ligands act as monodentate, coordinating through their α -nitrogen atoms. The complexes are non-ionic in benzene.

METAL complexes of azo compounds have received considerable attention in the past in view of their application as stable dye-stuffs¹. However, attention was devoted mostly to stable metal complexes, having greatly enhanced fastness properties. Thus, whereas the literature is extensive on *o,o'*-dihydroxyazo compounds and their metal chelates, very few reports exist on labile complexes of *o*-monohydroxyazo compounds¹. Hence this investigation on complexes of 1-phenylazo-2-naphthols (I) with iron(III) chloride was undertaken.

Six *o*-hydroxyazo ligands used by us formed lustrous black crystals with anhydrous iron(III) chloride in boiling dry benzene. These complexes are non-hygroscopic and could be recrystallized several times from benzene. The complexes have the composition $FeCl_3.L_2$ (Table 1). These are non-

ionic in benzene and hence may be represented as $[Fe(L)_2Cl_3]$.

Any deprotonation of the ligands during complex formation is ruled out since no hydrogen chloride could be detected in the effluent vapours from the reaction flask. It is thus evident that the phenylazonaphthols act as neutral ligands. Addition of aqueous caustic soda or mineral acid results in the decomposition of the complexes giving the ligands in almost quantitative yield.

Hydroxyazo compounds exhibit azo-hydrazone tautomerism². In the case of *o*-hydroxyazo compounds, the tautomers exist as strongly hydrogen bonded structures¹ (I) and (II), the latter predominating³. In accordance with structure (II), the infrared spectra of 1-phenylazo-2-naphthols show a band at $1610+10\text{ cm}^{-1}$, which may be attributed to the hydrogen bonded carbonyl group⁴. In keeping with the hydrogen bonded N—H...O structure, the X—H (X=N or O) band around 2400 cm^{-1} is broadened almost out of recognition. The X—H band remains unaltered in the metal complexes also, showing that the hydrogen bond persists in the complexed state. This is further corroborated by the fact that like the free ligands, the metal complexes also do not form any ammonium salt with dry ammonia in benzene. In view of the hydrogen bonded structure of the coordinated ligands, they may be expected to act only as monodentate ligands. Since the C=O stretching frequency of the ligands remains undepressed in the complexes, it is evident that the oxygen atom does not coordinate⁵.

It appears, therefore, that it is one of the nitrogen atoms of the ligand that is bonded to the

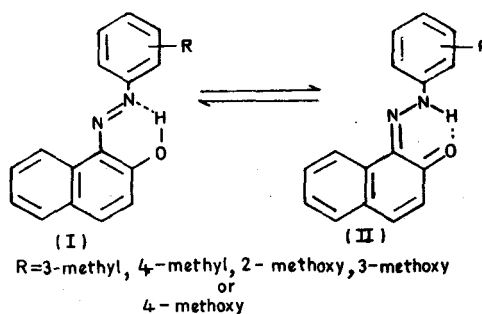


TABLE 1 — ANALYTICAL DATA OF THE COMPLEXES

Ligand (I) (R =)	m.p. (°C*)	Found (%)†				
		C	H	N	Fe	Cl
H	210	—	—	—	8.17 (8.48)	15.90 (16.11)
3-Methyl	200	59.58 (59.51)	4.39 (4.08)	8.57 (8.16)	8.00 (8.10)	14.95 (15.45)
4-Methyl	210	60.01	4.46	8.52	8.03	15.15
2-Methoxy	195	—	—	—	8.04 (7.78)	14.52 (14.72)
3-Methoxy	205	56.75 (56.82)	4.20 (3.90)	8.51 (7.80)	8.25	14.72
4-Methoxy	185	—	—	—	8.00	14.60

*Melt with decomposition; yield about 80%.

†Calculated values are given in parentheses. Calculated values for isomeric compounds are not mentioned.

metal. The spectrum of each complex resembles closely that of the corresponding ligand, except that a medium intensity band of the ligands at $1595 \pm 5 \text{ cm}^{-1}$ (attributable partly to aromatic skeletal vibrations and partly to $\nu\text{C}=\text{N}^6$ becomes more intense in the spectra of the complexes, probably due to coordination by the azomethine nitrogen atom of the ligand. Unlike $\nu\text{C}=\text{O}$, $\nu\text{C}=\text{N}$ is generally unaffected on coordination⁷, although variation in the intensity of absorption of the latter is observed⁸.

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References

1. PRICE, R., *The chemistry of synthetic dyes*, edited by K. Venkataraman, Vol. 3 (Academic Press, New York), 1970.
2. WILEY, R. H. & JARBDE (Jr), C. H., *J. Am. chem. Soc.*, **77** (1955), 403.
3. VENKATARAMAN, K., *The chemistry of synthetic dyes*, Vol. I (Academic Press, New York), 1952, 446.
4. BASSIGNANA, P. & COGROSSI, C., *Tetrahedron*, **20** (1964), 2861.
5. LAPPERT, M. F., *J. chem. Soc.*, (1961), 817.
6. SARMA, B. D., RAY, K. R., SIEVERS, R. E. & BAILAR (Jr), J. C., *J. Am. chem. Soc.*, **86** (1964), 14.
7. SARMA, B. D. & BAILAR (Jr), J. C., *J. Am. chem. Soc.*, **77** (1955), 5476.
8. BELLAMY, L. J., *The infrared spectra of complex molecules* (Methuen & Co., London), 1964, 268, 271.

Uranium(V) Complexes of Dibasic Tridentate & Tetradentate Schiff Bases

R. G. VIJAY & J. P. TANDON

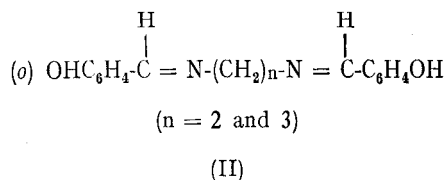
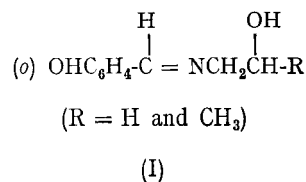
Department of Chemistry, University of Rajasthan
Jaipur 302004

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Schiff base complexes of uranium(V) of the types $\text{U}(\text{OC}_2\text{H}_5)_3(\text{SB})$, $\text{U}(\text{OC}_2\text{H}_5)_2(\text{SB})_2$, $\text{U}_2(\text{OC}_2\text{H}_5)_4(\text{SB})_3$, $\text{U}(\text{OC}_2\text{H}_5)_3(\text{S}_1\text{B}_1)$, $\text{U}(\text{OC}_2\text{H}_5)_2(\text{S}_1\text{B}_1)_2$ and $\text{U}_2(\text{OC}_2\text{H}_5)_4(\text{S}_1\text{B}_1)_3$ have been synthesized by the reactions of uranium(V) ethoxide with the dibasic tridentate (SBH_2) and dibasic tetradentate ($\text{S}_1\text{B}_1\text{H}_2$) Schiff bases in 1:1, 1:2 and 2:3 molar ratios (metal:ligand). On the basis of elemental analysis, molecular weight and IR spectral data, probable structures for the compounds have been indicated. The exchange reactions of U(V) complexes containing terminal ethoxy groups in the presence of excess *t*-butanol have also been carried out and the results show that the terminal ethoxy groups are labile in nature and undergo exchange reactions.

IN an earlier communication¹ we have reported uranium(V) complexes of monobasic bidentate Schiff bases derived from salicylaldehyde and alkylamines. However, reactions of dibasic tridentate or tetradentate Schiff bases with uranium(V) ethoxide have not been investigated earlier. We report here the reactions of uranium(V) ethoxide with dibasic tridentate ligands of the type $\text{SBH}_2(\text{I})$

having the donor system HO-N-OH and dibasic tetradentate ligands of the type $\text{S}_1\text{B}_1\text{H}_2(\text{II})$ having the donor system HO-N-N-OH .



The reactions were carried out under anhydrous conditions as the resulting Schiff base complexes of U(V) are moisture-sensitive. Uranium penta-ethoxide was prepared as described by Gilman *et al.*² and distilled before use [Found: U, 51.31; OC_2H_5 , 48.42. Calc. for $\text{U}(\text{OC}_2\text{H}_5)_5$: U, 51.40; OC_2H_5 , 48.60%].

Schiff bases of the type $\text{OHC}_6\text{H}_4\text{CH}=\text{NXOH}$ [$\text{X} = -\text{CH}_2\text{-CH}_2\text{-}$ or $-\text{CH}_2\text{CH}(\text{CH}_3)-$] were prepared³ by refluxing the stoichiometric amounts of salicylaldehyde and 2-hydroxy-ethylamine or 2-hydroxy-1-propylamine for several hours and then distilling the products before use. Schiff bases of the type $\text{OHC}_6\text{H}_4\text{CH}=\text{N}(\text{CH}_2)_n\text{N}=\text{CHC}_6\text{H}_4\text{OH}$ (where $n=2$ or 3) were prepared by heating the stoichiometric amounts of salicylaldehyde and ethylenediamine or 1,3-propylenediamine in absolute ethanol and the products were recrystallized.

Preparation of the complexes—To a solution of uranium penta-ethoxide in anhydrous benzene (~ 60 ml) was added the requisite amount of the Schiff base. After refluxing the reaction mixture, ethanol-benzene azeotrope and the excess of the solvent were fractionated off. The resulting brown or brownish-red solids were separated and analysed (Table 1).

Exchange reactions of Schiff base complexes with *t*-butanol—The Schiff base complexes and *t*-butanol were mixed in anhydrous benzene. After refluxing the reaction mixture, ethanol-benzene azeotrope was removed and the excess benzene distilled at a high reflux ratio. The resulting brownish-orange solids were separated and analysed (Table 2). The reactions were successful in the case of complexes containing terminal ethoxy groups. Complexes having only bridging ethoxy groups did not undergo exchange reactions even in the presence of excess *t*-butanol.

The dibasic tridentate Schiff bases (SBH_2) react with uranium penta-ethoxide in the ratios 1:1, 1:2 and 2:3 to give products of the types $\text{U}(\text{OC}_2\text{H}_5)_3(\text{SB})$, $\text{U}(\text{OC}_2\text{H}_5)_2(\text{SB})_2$ and $\text{U}_2(\text{OC}_2\text{H}_5)_4(\text{SB})_3$ respectively with the liberation of 2, 4 and 6 moles of ethanol. The dibasic tetradentate Schiff bases ($\text{S}_1\text{B}_1\text{H}_2$) also react with uranium penta-ethoxide in the ratios 1:1, 1:2 and 2:3 to give products $\text{U}(\text{OC}_2\text{H}_5)_3(\text{S}_1\text{B}_1)$, $\text{U}(\text{OC}_2\text{H}_5)_2(\text{S}_1\text{B}_1)_2$ and $\text{U}_2(\text{OC}_2\text{H}_5)_4(\text{S}_1\text{B}_1)_3$ with the liberation of 2, 4 and 6 moles of ethanol respectively.